

# Carbon isotopes of marl and lake sediment organic matter reflect terrestrial landscape change during the late Glacial and early Holocene (16,800 to 5,540 cal yr B.P.): a multiproxy study of lacustrine sediments at Lough Inchiquin, western Ireland

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**Abstract** A 7.6-m lake sediment core from a marl lake, Lough Inchiquin, records variation in landscape evolution from 16,800 cal yrs B.P. to 5,540 cal yrs B.P. We observe significant variations (up to 12‰) in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  values that are interpreted to reflect secular changes in lake water  $\delta^{13}\text{C}_{\text{DIC}}$  values that result from a regional landscape transition from barren limestone bedrock to a forested ecosystem. Lake water  $\delta^{13}\text{C}_{\text{DIC}}$  values are therefore influenced by two isotopically distinct sources of carbon: terrestrial organic material (−27.1 to −31.2‰VPDB)

via oxidized soil organic matter and weathered limestone bedrock (+3.4‰VPDB). Isotope excursions in lacustrine sediment records are forced not only by changes in productivity but also by changes in the terrestrial environment. This has profound implications for the interpretation of paleoclimate records derived from lacustrine sediment and suggests that selection of appropriate lakes can provide records of terrestrial change where other related records are not available.

**Keywords** Lake sediment · Carbon cycle · Paleovegetation · Paleoecology · Paleolimnology

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## Introduction

Lake sediment has long served as an archive of continental environmental change because it contains a myriad of isotopic, chemical, and biological proxies (e.g. Meyers and Ishiwatari 1993; Talbot 1990; Leng and Marshall 2004) that characterize changes in past climate and environments.  $\delta^{13}\text{C}$  profiles of lake sediment have become a critical tool for paleoclimate studies because lake carbon budgets are sensitive to climate. Variations in carbon budgets are preserved in lake sediment organic matter, mollusk shells, ostracodes, and carbonate mud (e.g. Leng and Marshall 2004). Lakes situated in carbonate bedrock are particularly valuable for paleoclimate investigations

because the sediment may consist of marl intermixed with several percent organic matter.

In this study, we present a suite of sedimentological, lithological, chemical, and isotopic proxies to evaluate the capability of lake sediment to serve as a sensitive recorder of terrestrial ecosystem variability. This study focuses on a lacustrine marl core, from the Burren region of county Clare, Ireland. The terrestrial ecosystem of the Burren region experienced significant transitions during the late Glacial and early Holocene, providing a unique perspective into the influence of the terrestrial ecosystem on  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values in lake sediment. This approach is not intended to ignore the importance of other mechanisms in controlling  $\delta^{13}\text{C}$  values of lake sediment, but rather is intended to emphasize forcing mechanisms that are not typically considered.

The information presented herein is the second of a two part series of a high-resolution late Glacial to early Holocene climate study at Lough Inchiquin. Part one addressed hydrologic variability in western Ireland as a function of climate change using oxygen isotope values of marl sediment (Diefendorf et al. 2006). Part two (this study), focuses on carbon isotope records preserved in the marl sediment. These two studies are carried out on the same cores, the same carbonate samples, and incorporate the same age model. All data from both studies are available online (see supplementary data). Additional studies will address other lakes in the Burren region (*in progress*).

## Background

### Study site

Lough Inchiquin is a 110 ha hard water lake located ~20 km inland of the Atlantic Ocean (Figs. 1, 2A) and 2 km northwest of the town of Corrofin, County Clare. Lough Inchiquin is located in the Burren: a region characterized by deeply weathered Carboniferous limestone with only a thin veneer of soil (several cm). In areas where the bedrock is exposed, vegetation (grasses and shrubs) is found only in fractures and depressions (Fig. 2b; Dickinson et al. 1964; Watts 1984). The extent of soil thickness and the exposure of the limestone in the past are not well

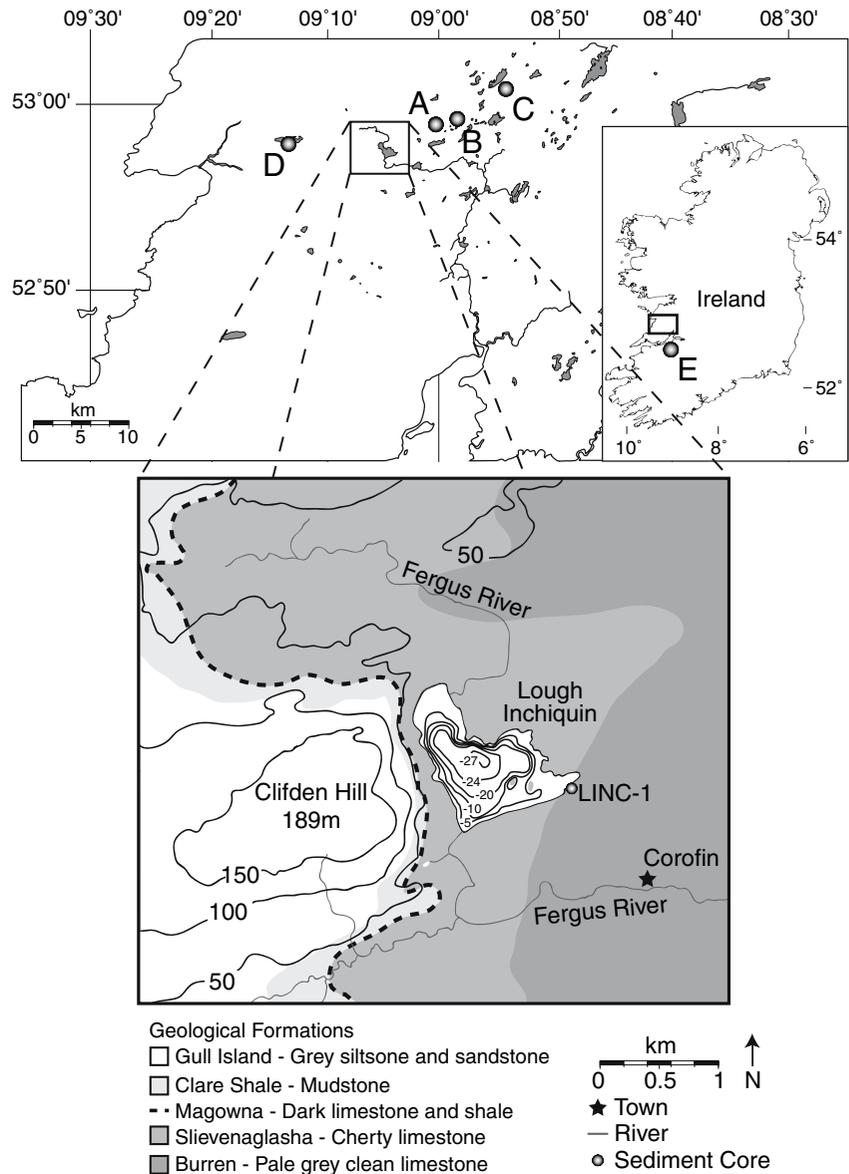
understood (Watts 1984), although it was sufficient to support a forest ecosystem (Watts 1963; Drew 1983). Lough Inchiquin has a mean depth of 10.8 m and a watershed area of 115 km<sup>2</sup> (Drew 1988). Thermal stratification is established in Lough Inchiquin by June despite strong winds, with isothermal conditions returning by mid-October (Allott 1986). This lake is hydrologically open with the River Fergus entering the lake from the north and exiting to the south. Water residence time is ~1 month (Irvine et al. 2001), making this lake ideal for high-resolution climate studies.

Lake sediment of the Burren region is typically composed of marl and/or organic rich material (e.g. peat, gyttja), overlying glacial sediments (e.g. Watts 1985). Marl originates primarily as charophyte calcite encrustations and to a smaller extent, ostracodes, mollusks, and gastropods. As this material accumulates, the resultant thick marl bench progrades towards the lake center.

### Vegetation history

Late Glacial and Holocene vegetation of the Burren region has been evaluated at several sites in western Ireland using palynology (Watts 1963, 1984, 1985; O'Connell et al. 1999). The closest sites, Lough Gortlecka and Lough Goller (Fig. 1), provide vegetation histories of the Late Glacial period (Watts 1963, 1985) and Lough Gortlecka and Rinn na Mona provide histories for the Holocene (Watts 1984). The terrestrial floral history can be generalized into 4 distinct periods: (1) a late Glacial bedrock landscape gradually colonized by herbaceous plants with minor *Betula* (Watts 1984); (2) a Younger Dryas (12.8–11.9 kyr B.P.) collapse of vegetation characterized by herbs, unstable soil and/or aeolian deposits (Watts 1985; Isarin et al. 1997) (3) a rapid post Younger Dryas recovery by pioneer vegetation as in period 1; and (4) establishment of trees in the early Holocene (Watts 1984). *Pinus sylvestris* (pine) and *Corylus* (hazel) forests were in place by 10.5 kyr B.P., followed by *Ulmus* (elm) and *Quercus* (oak), at 10 kyr B.P. with open ground persisting in places (Watts 1984). The establishment of *Pinus* in the Burren may have been the earliest recorded in western Ireland (Watts 1984). In spite of the presence of woodland at this time, there was still open ground

**Fig. 1** Map of Ireland, regional lakes of the Burren, and detailed map of Lough Inchiquin including geology and bathymetry (MacDermot et al. 2003; Allott pers. comm. 2004). Sites mentioned in text are Rinn na Mona (A), Lough Gortlecka (B), Poulroe (C), Lough Goller (D), and Tory Hill (E; O’Connell et al. 1999)



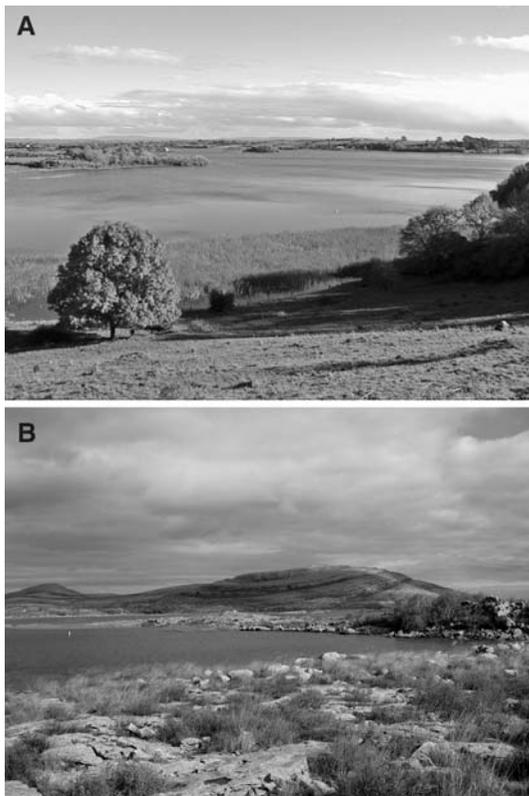
in places indicated by *Calluna* and *Pteridium* (Watts 1984).

**Materials and methods**

**Sample collection**

A 7.6-m square-rod piston core (LINC-1) was retrieved from the southeast shore of Lough Inchiquin (W09°04'44", N52°57'03"; Irish Grid number IR: 278

896) in July 2002 using a Livingstone square-rod piston-coring device (Fig. 1). Core sections were split longitudinally, visually described (Table 1), and subsampled for loss on ignition (LOI) at the Botany Department, National University of Ireland in Galway and at the Saskatchewan Isotope Laboratory. LOI determinations for weight percent total organic matter (TOM) and total calcite (TC) were made by roasting for 1 h at 550°C and 1,000°C (Fig. 3; Dean 1974), respectively, at 2.5 cm intervals (Fig. 3). LOI overestimates the total weight percent calcite in



**Fig. 2** (A) Lough Inchiquin from the northwest looking towards the coring site on the furthest shoreline. (B) Lough Gallaun (near Lough Gortlecka, Fig. 1) with Mullaghmore in the background exemplifies the unvegetated nature of the Burren region with exposed limestone bedrock. The landscape at Lough Inchiquin may have looked very similar in the late Glacial until the spread of terrestrial vegetation and later trees

clay-rich sediments due to water loss (3 to 4 wt. % water) from the crystalline lattice of clay minerals at 1,000°C (Dean 1974). Therefore, we interpret any %TC value below 5% as a true value of 0% calcite. Subsamples of the core were also processed for mineralogy using X-ray diffraction (XRD; Diefendorf 2005]. Samples of the underlying bedrock were collected for isotopic analysis. Modern terrestrial vegetation was also collected around the lake for a modern comparison.

#### Stable carbon isotope analyses

Samples for  $\delta^{13}\text{C}_{\text{calcite}}$  analysis (Fig. 4) were recovered as 0.5-mm slices at 1-cm intervals. Two samples from underlying bedrock were also analyzed. Prior to

analyses, macrofauna (e.g. gastropods) and microfaunal components (e.g. ostracodes) were removed by hand under a stereomicroscope to limit isotope analyses to fine-grained sediment. Samples were roasted in vacuo at 200°C for 1 h to remove volatile organics and water.  $\delta^{13}\text{C}_{\text{calcite}}$  values ( $n = 795$ ) were determined using standard analytical techniques (see Diefendorf et al. 2006) on a Thermo-Finnigan Kiel-III carbonate device coupled to a Thermo-Finnigan MAT 253 SIRMS (stable isotope ratio mass spectrometer) in the Saskatchewan Isotope Lab (SIL). Carbon isotope values are reported in delta notation relative to the standard Vienna Pee Dee Belemnite (VPDB):  $\delta^{13}\text{C} = 10^3[(^{13}\text{R}_{\text{sa}}/^{13}\text{R}_{\text{VPDB}})-1]$  where  $^{13}\text{R} = ^{13}\text{C}/^{12}\text{C}$  for samples (sa) and VPDB. Analyses were calibrated relative to NBS-18 and NBS-19. Reproducibility of  $\delta^{13}\text{C}_{\text{calcite}}$  is  $\pm 0.05\text{‰}$  based on repeat measurements of a standard ( $n = 58, 1\sigma$ ).

$\delta^{13}\text{C}_{\text{org}}$  values (Fig. 4) were determined from 2-mm slices at 2 to 3-cm intervals. Samples were sieved ( $<500 \mu\text{m}$ ) to remove larger terrestrial derived material. Calcite was removed from samples by acidification with 10% HCl in 50 ml centrifuge tubes for not more than 3 h. Samples were then centrifuged, supernatant decanted, washed with deionized water, and repeated until samples were neutral. Samples were dried in vacuo at 40°C for 2 h to remove moisture. Prior to analyses, samples were homogenized with a mortar and pestle. Additionally, 10 modern samples of local vegetation were collected. Modern samples (Table 2) were washed with deionized water, dried in vacuo at 40°C for 2 h, and subsequently homogenized with a mortar and pestle.  $\delta^{13}\text{C}_{\text{org}}$  analyses ( $n = 175$ ), as well as total organic carbon (TOC) and total nitrogen (TN), were determined via continuous flow on a Thermo-Finnigan Flash EA by oxidation at 1,000°C with chromium oxide followed by reduction to  $\text{CO}_2$  and  $\text{N}_2$  at 680°C.  $\text{CO}_2$  and  $\text{N}_2$  were subsequently passed through a 5 Å molecular sieve gas chromatograph at 50°C and then diluted with ultra pure He in a ConFlo III interface/open split.  $\text{CO}_2$  and  $\text{N}_2$  were measured on a Thermo-Finnigan MAT Delta Plus XL SIRMS in the SIL.  $\delta^{13}\text{C}_{\text{org}}$  values were normalized to the VPDB scale using a two-point calibration with well-defined internal standards and reproducibility is  $\pm 0.1\text{‰}$  ( $n = 45, 1\sigma$ ) based on repeated measurements of a sample. Carbon/nitrogen (C/N) ratios were determined from the molar ratios of TOC/TN and were

**Table 1** Lithostratigraphic description of the Lough Inchiquin sediment core LINC-1 (TC and TOM are total calcite and total organic matter from loss on ignition)

Age	Depth (m)	Description	TC (%)	TOM (%)
n.a. <sup>a</sup>	0.00–0.10	Dark brown peat with interbedded marl, plant roots	7–9	79–80
n.a. <sup>a</sup>	0.10–0.23	Yellowish–brown, sand interbedded with marl, numerous macrofossil fragments	71–86	5–14
n.a. <sup>a</sup>	0.23–0.55	Dark brown to black, gyttja or peat with macroscopic plant remains (gap in core occurred during coring due to compressibility of peat and large wood fragments)	4–75	20–89
5460–5770	1.00–1.25	Dark brown gyttja, highly fossiliferous	67–87	13–28
5770–6460	1.25–2.00	Brown to dark brown marl, macroscopic plant remains, fossiliferous	77–94	5–17
6460–6580	2.00–2.15	Dark brown, calcareous gyttja	61–88	9–32
6580–6920	2.15–2.60	Brown marl with some laminations, graded base contact	80–94	5–15
6920–8260	2.60–4.70	Grey/tan marl, macrofossils, minor amounts of macroscopic plant remains	73–94	5–20
8260–11420	4.70–6.44	Grey/tan marl, upward increase in macrofossils	51–95	3–14
11420–11610	6.44–6.58	Dark grey clay	4–7	8–9
11610–14750	6.58–7.21	Grey/tan marl	67–89	5–8
14750–14870	7.21–7.23	Dark grey clay, calcite and dolomite present (Diefendorf 2005)	46	9
14870–16280	7.23–7.47	Grey/tan marl	76–80	5–9
16280–16750	7.47–7.55	Gradation from dark grey to light grey calcite-rich, clay/silt, with coarse gravel	55–72	2–4

<sup>a</sup> Ages and all isotope data are omitted due to the gap in the core

<sup>b</sup> Loss on ignition is limited in high clay content soils due to 3–4 wt. % water loss from the crystal lattice of clay minerals at 1,000°C (Dean, 1974). Therefore, calcite content is likely zero. Also, samples in this interval did not produce CO<sub>2</sub> when reacted with phosphoric acid in the Kiel carbonate preparation device

corrected for inorganic nitrogen content (0.046%) following the methods of Talbot (2001).

### Radiocarbon dating

Age control was previously established by Diefendorf et al. (2006) by AMS <sup>14</sup>C dating of calcite and organic matter at the University of Arizona, converted to calendar years before 1950 (yr B.P.) using CALIB 4.3 (Stuiver et al. 1998), and corrected for a carbon reservoir effect. Additional details of the dating methods and the reservoir effect is discussed in detail by Diefendorf et al. (2006).

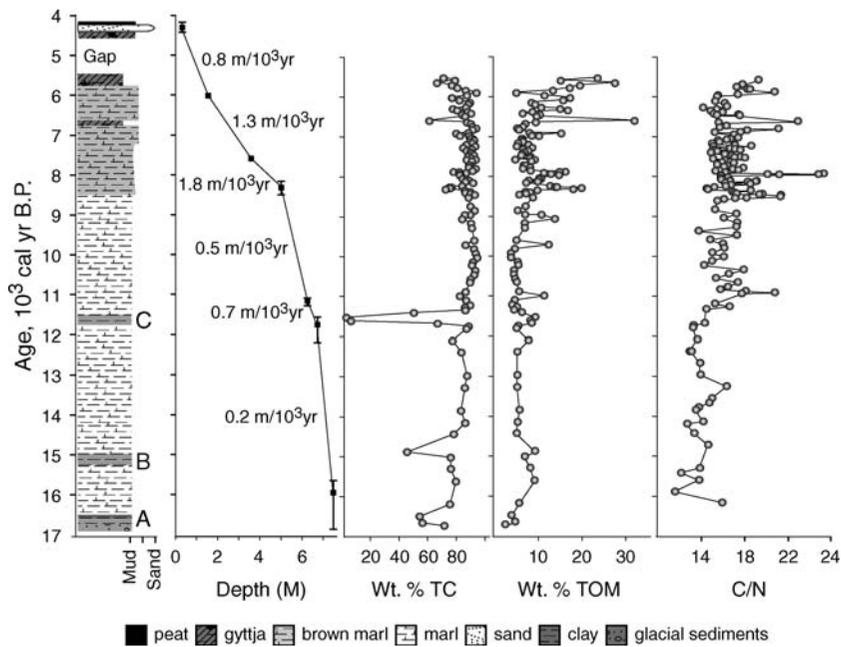
### Calculation of $\Delta\delta^{13}\text{C}$

Calculation of  $\Delta\delta^{13}\text{C}$  ( $=\delta^{13}\text{C}_{\text{calcite}}-\delta^{13}\text{C}_{\text{org}}$ ) is not entirely straightforward because  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  samples represent different periods of time due to sampling strategies for acquisition of sufficient

material for analyses (coarser sampling frequency of  $\delta^{13}\text{C}_{\text{org}}$ ). We choose therefore to calculate  $\Delta\delta^{13}\text{C}$  at depths where both  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  are measured instead of statistically interpolating values for  $\delta^{13}\text{C}_{\text{org}}$ . This does introduce some error into  $\Delta\delta^{13}\text{C}$  because we are comparing 0.5 mm  $\delta^{13}\text{C}_{\text{calcite}}$  samples to 2 mm  $\delta^{13}\text{C}_{\text{org}}$  samples. Thus, comparison of individual  $\Delta\delta^{13}\text{C}$  values is not possible, however long term trends in  $\Delta\delta^{13}\text{C}$  are still meaningful and are useful for interpretation of the data.

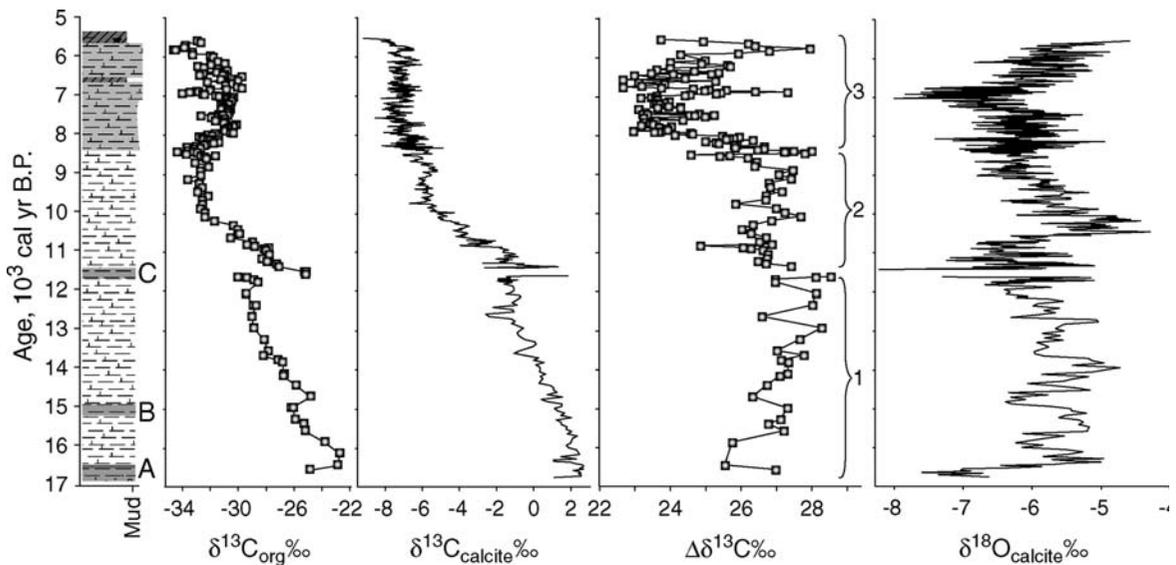
### Results

The lithostratigraphy for Lough Inchiquin from LINC-1 core (Table 1; Fig. 3) is primarily composed of marl with as much as 94% TC. The base of the core consists of glacial material overlain by alternating sequences of clay and marl with increasing organic material towards the top of the core. The gap



**Fig. 3** Lithostratigraphy (see Table 1 for descriptions), age model, wt. % total calcite (TC), wt. % total organic matter (TOM), and elemental C/N ratios versus cal yr B.P. A, B, C represent late Glacial, Older Dryas, and Younger Dryas clay deposits, respectively. The age model is from Diefendorf et al. (2006) and is based on AMS <sup>14</sup>C ages determined at the University of Arizona AMS facility. Ages are corrected for a

hard-water effect of 1575 <sup>14</sup>C yrs determined from measuring a coexisting sample of wood and calcite and ages are calibrated using Calib 4.3 (Stuiver et al. 1998). The age model is based on linear interpretation between calibrated radiocarbon ages. The 2σ calibrated age ranges are indicated with grey vertical bars when the error exceeds the black boxes



**Fig. 4** Lithostratigraphy,  $\delta^{13}C_{org}$ ,  $\delta^{13}C_{calcite}$ ,  $\Delta\delta^{13}C$ , and  $\delta^{18}O_{calcite}$  (from Diefendorf et al. 2006) versus cal yr B.P. Arrows 1, 2, 3 indicate general trends in  $\delta^{13}C_{org}$  and  $\delta^{13}C_{calcite}$

discussed in the text.  $\Delta\delta^{13}C$  ( $=\delta^{13}C_{calcite} - \delta^{13}C_{org}$ ) is calculated from horizons within the core where both calcite and organic samples were measured and are not interpolated

**Table 2** Various data for modern terrestrial plants, charophytes, peat, and Burren limestone bedrock (TOC is total organic carbon and TN is total nitrogen)

	$\delta^{13}\text{C}$ ‰ VPDB	$\delta^{15}\text{N}$ ‰ AIR	TOC (%)	TN (%)	C/N
<i>Organic matter analyzed</i>					
Poaceae	−27.1	3.1	45.6	2.1	25.1
Poaceae	−25.3	4.3	45.9	0.7	76.3
Poaceae <i>Danthonia</i>	−27.3	−1.1	46.4	0.3	199.2
<i>E. Calluna vulgaris</i>	−30.4	−4.5	47.5	1.3	44.2
<i>A. Acer pseudoplatanus</i>	−29.3	2.8	38.2	2.0	22.2
<i>P. Athyrium filix-femina</i>	−26.4	−0.9	43.1	0.6	85.8
<i>B. Alder glutinosa</i>	−29.5	−0.4	38.6	1.9	24.2
<i>C. Carex</i>	−30.6	3.0	43.5	1.7	30.6
<i>C. Carex</i>	−30.2	1.1	43.1	1.4	35.4
Unidentified shrub	−31.7	1.3	46.9	2.0	26.9
Chara #1	−39.0	5.5	42.8	3.7	13.5
Chara #2 (stem)	−43.5	6.9	46.0	1.3	39.9
Chara #2 (leaves)	−38.4	6.3	43.5	4.4	11.6
Chara #3	−35.9	5.0	42.8	3.2	15.8
Chara #4	−42.3	6.1	45.1	2.4	22.2
Chara #5 (large leaf)	−41.5	6.4	44.5	2.1	24.2
Chara #5 (small leaf)	−28.7	5.0	41.9	3.3	14.8
Peat (4,250 cal yr B.P.)	−29.1	4.2	47.4	3.0	18.5
Peat (4,275 cal yr B.P.)	−29.2	3.8	46.4	3.1	17.6
<i>Calcite material analyzed</i>					
Chara 1	−9.1				
Chara 2	−8.7				
Chara 3	−8.8				
Chara 4	−8.8				
Burren Limestone (Inchiquin)	3.4				
Burren Limestone (Inchiquin)	3.3				
Burren Limestone (Gortlecka)	3.2				
Burren Limestone (Gortlecka)	3.4				
Burren Limestone (Gortlecka)	3.6				

in the upper 1 m of core (Fig. 3) was caused by the high compressibility of peat as well as a large piece of wood (similar compressibility was observed in a second nearby core; data not presented). Because we cannot constrain the compressibility of the peat, we have chosen to omit all data for this section of core.

XRD samples for the marl-rich sections contained calcite with no aragonite or dolomite (Diefendorf 2005). Samples from the clay sections were primarily quartz and clay minerals. A clay sample at 14.8 kyr B.P. (7.22 m) contains dolomite as well. Visual inspection of the marl indicates that the calcite is

primarily fine-grained. The morphology of the marl sediment sampled at several horizons within the core is characterized by mm-scale tubular shaped casts, likely from the calcite encrustations on charophyte stems that are commonly observed in marl sediments (e.g. Hammarlund et al. 1997).

Lake sediment spanning the period between 16,800 yrs B.P. and 5,540 yrs B.P. displays large variation in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  values of up to  $\sim 11.9\%$ , with highest values in the oldest sediment. The marl directly overlying glacial sediment (A in Fig. 4) yields  $\delta^{13}\text{C}_{\text{calcite}}$  values of  $\sim 2.7\%$ , close to

the  $\delta^{13}\text{C}$  value of the limestone bedrock (3.4‰).  $\delta^{13}\text{C}_{\text{calcite}}$  values decrease upward from the base of the core toward a clay layer deposited  $\sim 15$  kyr B.P. (B in Fig. 4) that is interpreted to reflect the Older Dryas cold event (Diefendorf et al. 2006). At this level there is also a small positive excursion in  $\delta^{13}\text{C}_{\text{org}}$  values. Positive  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  excursions occur within the clay layer deposited between 11.4 kyr B.P. and 11.6 kyr B.P., coincident with the Younger Dryas (YD) cold event (C in Fig. 3).

The main feature observed in the  $\delta^{13}\text{C}_{\text{calcite}}$  profile is a trend towards lower values between clay layers that abruptly reverses immediately below the YD clay layer and increases by 3.2‰ before the signal is lost in the low TC content of the clay. In contrast, low  $\delta^{13}\text{C}_{\text{org}}$  values are found in both the marl and clay, though the resolution of the  $\delta^{13}\text{C}_{\text{org}}$  profile is lower, and the last measured  $\delta^{13}\text{C}_{\text{org}}$  sample below the clay layer yields a  $\delta^{13}\text{C}_{\text{org}}$  value of  $-30$ ‰. We observe a positive 5‰ shift in  $\delta^{13}\text{C}_{\text{org}}$  values above the clay layer to an average value of  $-25.2$ ‰ followed by a decrease to pre-excursion values by 11.3 kyr B.P.

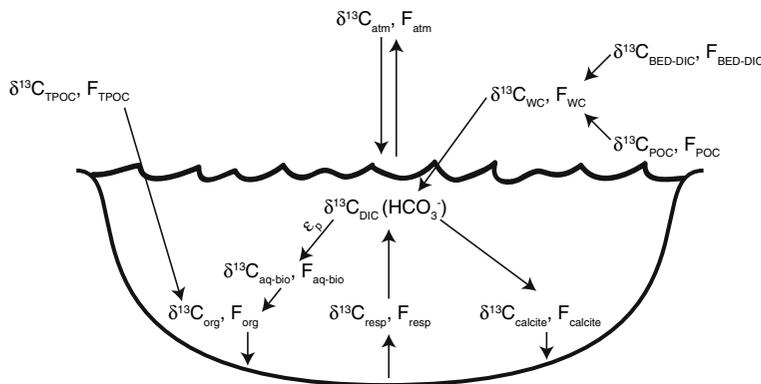
Following the YD,  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values continue to decrease for  $\sim 2$  kyrs until the base of an interval of brown marl is reached at 8.5 kyr B.P. lasting for  $\sim 4$  kyrs and overlain by peat. The  $\delta^{13}\text{C}_{\text{calcite}}$  profile through the brown marl interval features a large negative excursion of  $\sim 2$ ‰ in contrast to  $\delta^{13}\text{C}_{\text{org}}$  values that display a positive excursion over the same interval.

The main features of the  $\Delta\delta^{13}\text{C}$  secular record are three positively trending intervals. The first interval

(Interval 1, Fig. 4) from the base of the core to the YD-clay layer with an average  $\Delta\delta^{13}\text{C}$  value of  $27.2 \pm 0.7$ ‰, the second interval (Interval 2, Fig. 4) from the grey marl between the YD clay layer and the bottom of the brown marl with an average  $\Delta\delta^{13}\text{C}$  value of  $26.6 \pm 0.7$ ‰. The third interval (Interval 3, Fig. 4) begins at the base of the increase in TOM and C/N, coupled with a slight darkening in color coeval with an abrupt 5‰ decrease in  $\Delta\delta^{13}\text{C}$  values from 28‰ to 23‰. The main features of the darker marl interval are the slightly increasing  $\Delta\delta^{13}\text{C}$  values and increased variability in  $\delta^{13}\text{C}_{\text{org}}$ , TOM, C/N ratios, and  $\delta^{18}\text{O}_{\text{calcite}}$ . The change in the marl color may correlate with a change to more eutrophic conditions that is suggested by ostracode population changes (N. Tibert, pers. comm.).

Variation in C/N (molar) ratios are similar to the  $\Delta\delta^{13}\text{C}$  pattern at least until 8.5 kyr B.P. C/N ratios are lowest ( $<14$ ) between the bottom of the core and YD clay layer. C/N ratios range between 14 and 18 in the grey marl interval extending from the YD clay layer to the base of the brown marl. Baseline C/N ratios are similar in the overlying darker marl, but this interval is characterized by greater variability in C/N ratios with numerous spikes to values as high as 24.

Modern terrestrial organic matter (Table 2) from the Burren region is characterized by  $\delta^{13}\text{C}_{\text{org}}$  values between  $-25.3$ ‰ and  $-31.7$ ‰ and C/N ratios above 22.2. Charaphytes also have high C/N ratios ( $20 \pm 10$ ;  $n = 5$ ) but low  $\delta^{13}\text{C}$  values of  $-38.5 \pm 0.7$  ( $n = 5$ ). Peat isolated from  $\sim 4.2$  kyr B.P. has  $\delta^{13}\text{C}_{\text{org}}$  of  $-29.1$  and a C/N value of  $\sim 19$ .



**Fig. 5** Carbon cycle illustration/model for freshwater lake systems. The abbreviations are as follows: flux (F), atmosphere (ATM), dissolved inorganic carbon (DIC), limestone bedrock derived DIC (Bed-DIC), weathered carbon (WC), particulate

organic carbon (POC), terrestrial POC (TPOC), bulk organic sediment (ORG), aquatic derived primary productivity (Aq-prod), respired  $\text{CO}_2$  from sediment (resp), photosynthetic fractionation during primary production ( $\epsilon_p$ )

## Lacustrine carbon dynamics

### The qualitative model

We present a model of carbon dynamics of a lacustrine system (Fig. 5) that describes processes that can modify  $\delta^{13}\text{C}$  values of dissolved inorganic carbon (DIC;  $\delta^{13}\text{C}_{\text{DIC}}$ ) and explains the large covariant trends in  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$ . This model is applicable to other hard water lakes in limestone regions. This qualitative model builds on previous models and includes three significant sources of exogenous carbon: oxidized particulate organic carbon (POC), terrestrial particulate organic carbon (TPOC) and carbon weathered (WC) from bedrock and the oxidation of organic matter; these components are infrequently discussed in lake carbon models (e.g. Hammarlund et al. 1997; Jones et al. 1998; Leng and Marshall 2004; Pace et al. 2004).  $\delta^{13}\text{C}_{\text{DIC}}$  values of hard-water lakes are primarily controlled by changes in the inorganic and organic carbon flux into the lake, primary productivity, organic matter burial, heterotrophic respiration, TPOC, calcite burial and dissolution, and  $\text{CO}_2$  equilibration with the atmosphere. These components are represented in Fig. 5 and are discussed subsequently.

The inorganic carbon weathering flux consists of two primary components: DIC and oxidized POC (particulate organic carbon) ( $F_{\text{WC}}$ ; Fig. 5), that represent external sources of oxidized carbon that influence lake  $\delta^{13}\text{C}_{\text{DIC}}$ . The terrestrial DIC input is derived from stream water, rainfall, groundwater, and snowmelt. Variations in the magnitude of the terrestrial DIC-flux are limited by calcite equilibria, but the  $\delta^{13}\text{C}$  value of  $F_{\text{WC}}$  ( $\delta^{13}\text{C}_{\text{WC}}$ ) varies more widely as it is regulated by contributions from two isotopically distinct sources: (1) limestone bedrock ( $\delta^{13}\text{C} = 3.4\text{‰}$ , this study), and (2)  $\text{CO}_2$  derived from the oxidation of POC and/or dissolved organic carbon. POC is derived from soil and terrestrial organic matter (leaf litter;  $\sim -25\text{‰}$  to  $-32\text{‰}$  for  $\text{C}_3$  taxa in Ireland, supplemental data) and the oxidation of POC that occurs primarily during heterotrophic degradation by bacteria and fungi. POC oxidation generates soil- $\text{CO}_2$  that can equilibrate with surface waters and alter the  $\delta^{13}\text{C}_{\text{DIC}}$  that is supplied to lakes via the  $F_{\text{WC}}$ . Dissolved organic carbon will have a similar effect and is included in the  $F_{\text{WC}}$ . Carbon isotope fractionation

associated with this transformation from organic matter to soil- $\text{CO}_2$  is not well understood; however, it is assumed that  $\delta^{13}\text{C}_{\text{org}}$  values are not significantly affected by heterotrophic respiration (Cerling 1984; Quade et al. 1989; Šantrůčková et al. 2000; Ehleringer et al. 2000). POC that is not oxidized to DIC is discussed below and is operationally defined as terrestrial POC (TPOC).

Primary productivity provides a sink for DIC in lake systems. During the growing season, primary productivity in the epilimnion elevates  $\delta^{13}\text{C}_{\text{DIC}}$  because of preferential uptake of  $^{12}\text{C}$  during photosynthesis (McKenzie 1985; Hollander and McKenzie 1991; Bade et al. 2004; Leng and Marshall 2004). This carbon isotope fractionation is related to the availability of  $\text{CO}_{2(\text{aq})}$  in the water column. As  $[\text{CO}_{2(\text{aq})}]$  decreases, the photosynthetic fractionation factor ( $\epsilon_p$ ) decreases, reducing the isotopic offset between  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}$  of aquatic biomass ( $\delta^{13}\text{C}_{\text{aq-bio}}$ ; see Royer et al. 2001). This mechanism is complicated by vegetation that actively utilizes  $\text{HCO}_3^-$  (Laws et al. 1995; Popp et al. 1998), thereby explaining high  $\delta^{13}\text{C}_{\text{calcite}}$  values for the calcareous algae *Chara* (e.g. McConnaughey 1991; McConnaughey and Falk 1991; Hammarlund et al. 1997), that are a significant component of the aquatic biomass at Lough Inchiquin. The degree to which this affects bulk  $\delta^{13}\text{C}_{\text{org}}$  values is not known.

Heterotrophic respiration ( $F_{\text{resp}}$ ; Fig. 5) of organic matter in lake sediment is another source of inorganic carbon as  $\text{CO}_2$  is liberated during organic matter degradation. Respiration is important in recycling nutrients that are buried in lake sediment. The portion of buried organic matter that is returned via respiration is difficult to constrain, but in marine systems, almost 99% is recycled, even in anoxic environments (Hedges and Oades 1997). The  $\delta^{13}\text{C}$  value of respired  $\text{CO}_2$  is difficult to constrain and is a function of the degree of anoxia, which regulates the mode of microbial degradation, and therefore the degree of  $^{13}\text{C}$ -fractionation. Respired carbon decreases  $\delta^{13}\text{C}_{\text{DIC}}$  values in the hypolimnion in stratified lakes (e.g. Quay et al. 1986; Bade et al. 2004; Leng and Marshall 2004).

TPOC ( $F_{\text{TPOC}}$ ; Fig. 5) is delivered to the lake predominantly by air and water. TPOC is different than POC because it is not oxidized and therefore does not influence  $\delta^{13}\text{C}_{\text{DIC}}$  values. TPOC is also compositionally very different than aquatic organic

matter, containing compounds such as lignin that are resistant to decay, especially in lakes, because they are only degraded by basidiomycete fungi and certain bacteria (e.g. Glaser 2005; Gleixner 2005). Labile TPOC (e.g. simple carbohydrates, amino sugars, proteins) will be similar to aquatically produced organic matter and is likely subject to microbial respiration. TPOC may include some fraction of kerogen from the limestone bedrock (Blair et al. 2003) but can likely be ignored for purposes of this study because of the small amount of kerogen in the surrounding bedrock.

Calcite is produced by a variety of aquatic organisms such as charaphytes, algae, ostracodes, and gastropods. At Lough Inchiquin, calcite is dominantly produced by *Chara* as observed by the abundance of coarse-grained calcite within the sediment with characteristic *Chara* morphologies and the presence of *Chara* gyrogonites.  $\delta^{13}\text{C}_{\text{calcite}}$  will be dependant on the  $\delta^{13}\text{C}_{\text{DIC}}$  value and on the carbon isotope fractionation ( $\text{HCO}_3^-$  to calcite), which is temperature dependant ( $\sim 1\text{‰}$  from  $5^\circ\text{C}$  to  $25^\circ\text{C}$ ; Mook 1986). As previously mentioned,  $\text{HCO}_3^-$  uptake by *Chara*, via active transport, may cause an increase in  $\delta^{13}\text{C}_{\text{calcite}}$  values associated with proton pumping by *Chara* (McConnaughey 1991; McConnaughey and Falk 1991; Hammarlund et al. 1997). The degree to which active transport is significant in long-term studies of lake sediments is likely not important as long as there are no major changes in biomass communities, such as a change from calcite predominantly produced by *Chara* to calcite produced by dominantly by another organism. We do not observe such a change at Lough Inchiquin. The influence of calcite dissolution can be ignored in this hard-water lake because it was likely always saturated with respect to  $\text{HCO}_3^-$ .

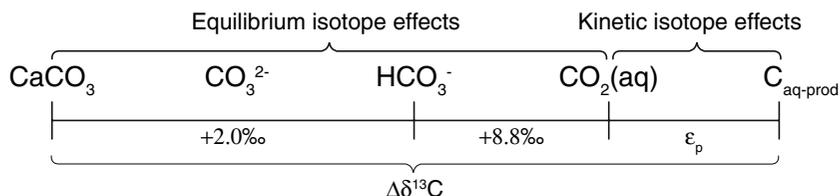
Atmospheric  $\text{CO}_2$  ( $F_{\text{atm}}$ ; Fig. 5) influences lake  $\delta^{13}\text{C}_{\text{DIC}}$  values directly via atmospheric  $\text{CO}_2$

( $\delta^{13}\text{C} = \sim -7$  to  $-8\text{‰}$ ) exchange at the air-water interface, and indirectly through terrestrial weathering reactions.  $\text{CO}_2$  exchange is a function of equilibration, that is dependant on many factors such as carbonate equilibria, temperature, atmospheric  $p\text{CO}_2$ , and water column mixing (e.g. Leng and Marshall 2004).

Carbon isotope variation:  $\Delta\delta^{13}\text{C}_{\text{calcite-org}}$

Previous studies have used the difference between  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  ( $\Delta\delta^{13}\text{C}$ ) for estimation of  $\varepsilon_p$  (Arthur et al. 1985; Kump and Arthur 1999), to infer  $[\text{CO}_{2(\text{aq})}]$  in marine environments and to determine paleo- $p\text{CO}_2$  (see Royer et al. 2001 for review). This has been applied to the lacustrine environments to infer subseasonal changes in  $[\text{CO}_{2(\text{aq})}]$  that result from productivity (Hollander and McKenzie 1991).  $\Delta\delta^{13}\text{C}$  is a powerful tool for interpreting carbon dynamics in lacustrine environments because  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  are both related to  $\delta^{13}\text{C}_{\text{DIC}}$  (Figs. 5, 6). Decreases in  $\Delta\delta^{13}\text{C}$  are demonstrated to correlate with decreasing  $\text{CO}_{2(\text{aq})}$  (O'Leary 1981; Farquhar et al. 1989; Hollander and McKenzie 1991; Hollander et al. 1992) and reflect the  $[\text{CO}_{2(\text{aq})}]$  in surface waters where calcite is formed and organic matter is produced.

$\delta^{13}\text{C}_{\text{org}}$  values are offset from the record of  $\delta^{13}\text{C}_{\text{calcite}}$  values by a fractionation factor that reflects carbon fixation during photosynthesis by primary producers (Figs. 5, 6). If the suite of primary producers changes, or if  $\varepsilon_p$  changes due to variations in  $[\text{CO}_{2(\text{aq})}]$ , this will alter the  $\delta^{13}\text{C}_{\text{DIC}}$  values and result in a shift in  $\Delta\delta^{13}\text{C}$ . However, on longer timescales, the subseasonal variation in  $\varepsilon_p$  becomes less significant, and is influenced by long-term changes in  $[\text{CO}_{2(\text{aq})}]$  as a function of  $p\text{CO}_2$  and calcite equilibria. The small change in Holocene  $p\text{CO}_2$  values should have a minimal effect on  $[\text{CO}_{2(\text{aq})}]$  considering the small change in  $p\text{CO}_2$



**Fig. 6** Illustration of carbon isotope relationships between organic matter and calcite sediments (modified from Royer et al. 2001). Fractionation values for illustration purposes are calculated at  $25^\circ\text{C}$  (Mook et al. 1974; Mook 1986)

(e.g. Indermühle et al. 1996). Large changes in  $\Delta\delta^{13}\text{C}$  are likely affected by changes in  $\delta^{13}\text{C}_{\text{org}}$  that are a mixed component between autochthonous biomass and exogenous sources of carbon, such as TPOC. Thus,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  profiles should co-vary precisely if both are responding only to changes in  $\delta^{13}\text{C}_{\text{DIC}}$  values in the lake through time, in which case  $\Delta\delta^{13}\text{C}$  should be invariant without the addition of TPOC. The presence of TPOC in lake sediments may be reflected by  $\delta^{13}\text{C}_{\text{org}}$  values of total organic carbon if the TPOC is isotopically distinct from aquatic organic matter. TPOC is significant because if, for example, the entire  $F_{\text{POC}}$  contribution were buried in lake sediment before oxidation could occur, no change in lake  $\delta^{13}\text{C}_{\text{DIC}}$  would result, and no signature of this flux would be imparted to sedimentary calcite preserved in sediment. In such cases, independent behavior between  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  profiles should be observed in  $\Delta\delta^{13}\text{C}$  values (e.g. Hammarlund et al. 1997; Pace et al. 2004). This influence of TPOC on  $\Delta\delta^{13}\text{C}$  can explain variations of several ‰ and smaller change is likely related factors that affect  $\varepsilon_p$ .

## Discussion

The base of the core preserves a transition from glacial sediment to lake marl (A in Fig. 4) at 16,800 yrs B.P. From 16,800 yrs B.P. to 16,300 yrs B.P., lake sediment yields  $\delta^{13}\text{C}_{\text{calcite}}$  values of  $\sim 2.7\text{‰}$  and  $\delta^{18}\text{O}_{\text{calcite}}$  values that range between  $-7.6\text{‰}$  and  $-5.0\text{‰}$  VPDB.  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{18}\text{O}_{\text{calcite}}$  values may reflect an input of detrital calcite with values of  $\delta^{13}\text{C}_{\text{bedrock-calcite}}$  and  $\delta^{18}\text{O}_{\text{bedrock-calcite}}$  of 3.4 and  $-10.8\text{‰}$ , respectively. Therefore, the rapid increase in  $\delta^{18}\text{O}_{\text{calcite}}$  values from 16,800 yrs B.P. to 16,300 yrs B.P. could reflect a mixing between detrital and autochthonous calcite (Diefendorf et al. 2006) with rapidly decreasing proportions of detrital calcite towards 16,300 yrs B.P. However, if a detrital signal is modifying  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{18}\text{O}_{\text{calcite}}$  at this interval, the  $\delta^{13}\text{C}_{\text{DIC}}$  value must be similar to bedrock  $\delta^{13}\text{C}$  values in order to explain the high  $\delta^{13}\text{C}_{\text{org}}$  values.

$\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  values decrease in tandem from 16.2 kyr B.P. to 8.5 kyr B.P. The general covariance between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  must be in response to changing  $\delta^{13}\text{C}_{\text{DIC}}$  values, rather than other factors such as productivity. From 16.2 kyr B.P.

to 8.5 kyr B.P., pollen evidence from nearby lakes indicates an increase in the distribution, density, and diversity of terrestrial plants (Watts 1963, 1984). Therefore, we interpret the 9‰ decrease in  $\delta^{13}\text{C}_{\text{DIC}}$  values to reflect post-glacial expansion of the terrestrial biomass. The establishment and expansion of terrestrial biomass generated an increase in organic detritus, the subsequent development of soils, and concomitant increases in soil organic matter and dissolved organic carbon. Soil organic matter and soil-respired  $\text{CO}_2$  from the oxidation of soil organic matter provides  $\delta^{13}\text{C}$  values of  $-30$  to  $-25\text{‰}$  (Cerling 1999). The oxidation of soil organic matter and terrestrial detritus lowers  $\delta^{13}\text{C}_{\text{POC}}$  values (Fig. 5) thereby decreasing  $\delta^{13}\text{C}_{\text{WC}}$  (bedrock and terrestrial organic matter) and subsequently the  $\delta^{13}\text{C}_{\text{DIC}}$  that is transferred to  $\delta^{13}\text{C}_{\text{aq-bio}}$ , and recorded by  $\delta^{13}\text{C}_{\text{org}}$ , and  $\delta^{13}\text{C}_{\text{calcite}}$ . Therefore, highest  $\delta^{13}\text{C}$  values at the base of the core reflect a poorly vegetated landscape of exposed limestone where lake water  $\delta^{13}\text{C}_{\text{DIC}}$  is primarily controlled by  $\delta^{13}\text{C}_{\text{WC}}$  from weathered limestone bedrock ( $\delta^{13}\text{C}_{\text{bed-DIC}} = +3.4\text{‰}$ ). As the floral density increases with time, the carbon flux from limestone weathering becomes increasingly diluted by the  $F_{\text{POC}}$  (Fig. 5) from soils. Isotope exchange with the atmosphere could also explain these high values, however it cannot explain the decreasing trends through time.

The amount of soil organic matter and terrestrial detritus must be sufficient to mask the increased weathering of limestone from the increased dissolution of calcite by humic acids from the decomposition of terrestrial biomass. Therefore, the large millennial-scale trends in  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  profiles of Lough Inchiquin are best explained as shifts in the isotope values of two distinct sources of carbon supplied to the lake by limestone weathering and the establishment and subsequent supply of oxidized soil organic matter to the lake water. Smaller decadal shifts in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  are caused by changes in aquatic productivity, aquatic respiration, and algal isotopic fractionation.

The YD event occurred within the generally decreasing values between 16.2 kyr B.P. and 8.5 kyr B.P. and is associated with a clay layer (C in Figs. 4, 5). Prior to the emplacement of the clay layer is a rapid increase in  $\delta^{13}\text{C}_{\text{calcite}}$  values and a rapid decrease in  $\delta^{18}\text{O}_{\text{calcite}}$  values that are most likely explained by detrital calcite from the local

bedrock from increased weathering associated with severe climate conditions in western Ireland (e.g. Watts 1963, 1984; O'Connell et al. 1999). The late deposition of clay in the YD is not observed at other sites in western Ireland and it is conceivable that the age model may not adequately account for the very low sedimentation rates during the deposition of the clay, and it is possible that that the whole of the YD climate event is represented by the clay interval. However,  $\delta^{18}\text{O}_{\text{calcite}}$  values suggest that the YD begins much earlier in the record, consistent with established ages for the YD, suggesting an intensification of cold/dry climate late in the YD in western Ireland (Diefendorf et al. 2006). The YD clay layer does not contain calcite, consistent with observations at other sites in western Ireland (Watts 1963, 1984, 1985), likely due to low summer temperatures (e.g. O'Connell 1999) and low lake productivity limiting the biological precipitation of calcite.

Following the YD clay layer,  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  are relatively high, similar to those at the base of the core. The return to high values suggests that  $\delta^{13}\text{C}_{\text{DIC}}$  values are again dominated by the  $\delta^{13}\text{C}_{\text{WC}}$  signal that is regulated primarily by limestone bedrock, although there may be some atmospheric component as well. The primary plant communities are herbaceous plants and grasses with decreased soil stability (Watts 1984), again suggesting minimal input of oxidized soil organic matter. After the YD event, the lake carbon cycle shifted back to pre-excursion  $\delta^{13}\text{C}$  values over an interval of  $\sim 1,700$  years, commensurate with the establishment of a pioneer vegetation and subsequent development of a forest community.

Using  $\delta^{13}\text{C}$  values as an index of the state of the terrestrial ecosystem, a further 5‰ decrease in the post YD interval reflects progressive development of soils and expansion of the terrestrial biomass following the YD cold period.  $\delta^{13}\text{C}$  values track the transition from a sparsely vegetated post-glacial landscape with poor soil development, to a more modern landscape of forests and mature soils, unlike the modern soils of the Burren region (Watts 1984). Pollen records support significant increases in pine, oak, hazel, and elm at  $\sim 10$  kyr B.P. at nearby Lough Gortlecka (Watts 1985), reaching their maximum density by 8.5 kyr, coincident with the transition from the grey to brown marl, and end of the long post-glacial decline in lake sediment  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values.

Although the importance of  $\delta^{13}\text{C}_{\text{WC}}$  in driving large variations in  $\delta^{13}\text{C}_{\text{DIC}}$  is apparent, it is clearly not the only control on  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values. At 8.5 kyr B.P.  $\delta^{13}\text{C}_{\text{org}}$  values are as low as  $\sim -34\%$  likely reflecting not only low  $\delta^{13}\text{C}_{\text{DIC}}$  values, but possibly either a change in the relative contributions of primary organic matter producers in the lake, such as a shift in the proportions of algae to *Chara* dominated sediment, or an increase in  $\delta^{13}\text{C}_{\text{resp}}$  from the release of  $\text{CO}_2$  from methanogenesis. Modern *Chara* have  $\delta^{13}\text{C}_{\text{org}}$  values in this range and this interpretation is also supported by the presence of *Chara* fragments and gyrogonites found in the sediment (Diefendorf, A., unpublished data).

We interpret two intervals of slightly increasing  $\Delta\delta^{13}\text{C}$  trends: (1) from the base of the core to the YD clay layer (Interval 1, Fig. 4), and (2) from the YD clay layer to base of the brown marl at 8.5 kyr B.P. (Interval 2, Fig. 4), as reflecting, at least in part, increased contributions of TPOC to the lake sediment as the terrestrial biomass recovered and expanded following severe climate disturbances associated first with glaciation, and second the YD cold period.

Above 8.5 kyr B.P., a major change/reorganization of the lake is indicated by changes in lithostratigraphy, increased C/N ratios, a brief increase in TOM, increased variation in  $\delta^{13}\text{C}_{\text{calcite}}$  values, an increase in  $\delta^{13}\text{C}_{\text{org}}$  values, and a rapid decrease in  $\Delta\delta^{13}\text{C}$ . Interval 3 (Fig. 4) is characterized by a decoupling of trends in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$  that characterized the core up to 8.5 kyr B.P., suggesting that above 8.5 kyr B.P.  $\delta^{13}\text{C}_{\text{org}}$  is not in equilibrium with  $\delta^{13}\text{C}_{\text{DIC}}$ , as indicated by the minimal change in  $\delta^{13}\text{C}_{\text{calcite}}$ . The large decrease in  $\Delta\delta^{13}\text{C}$  from 28‰ to 23‰ beginning at 8.5 kyr B.P. is caused by increasing  $\delta^{13}\text{C}_{\text{org}}$  values and decreasing  $\delta^{13}\text{C}_{\text{calcite}}$  values, clearly demonstrative of decoupling between the  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$ . Therefore, the change that occurs in the lake at this time must primarily affect the bulk organic sediment. The most plausible explanation would be a shift from a *Chara* dominated organic source to a new aquatic source, possibly a marginal aquatic succession such as a fen/peat type source producing an increased proportion of the organic sediment. This is supported by the C/N ratios and  $\delta^{13}\text{C}$  values we measured on peat samples at  $\sim 4.3$  kyr B.P. (Table 2) as well as the slight increase in TOM. Another possible explanation is an increase

in TPOC because  $\delta^{13}\text{C}_{\text{org}}$  values are more similar to terrestrial vegetation values (Table 2). C/N ratios do not support a large increase in terrestrial organic material, however the use of C/N values as a tracer of source is shown to be limited in other environmental settings (Sauer et al. 2001). Pollen evidence suggests that this period is likely a woodland type vegetation that evolved about 10 kyr B.P. (Watts 1984).

In addition to the changes in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{calcite}}$ ,  $\delta^{18}\text{O}_{\text{calcite}}$  values at  $\sim 8.5$  kyr B.P. record an abrupt increase subsequently followed by a decrease in values interpreted by Diefendorf et al. (2006) to represent a cool/cold period associated with the “8.2 ka cold event” (Alley et al. 1997) observed elsewhere in Europe (e.g. McDermott et al. 2001; Magny and Bégeot 2004). This cold period is associated with a decrease in precipitation in western Ireland (McDermott et al. 2001; Baldini et al. 2002) and possibly a decrease in lake water level (Diefendorf et al. 2006). The change in lake water level may also support the idea that the aquatic vegetation is changing, possibly to a shallower, more fen like vegetation. The hypothesis of a transition in vegetation related to more eutrophic conditions is supported by changes in ostracode assemblages (Tibert, N., pers. comm.).

A rapid decrease in  $\delta^{13}\text{C}_{\text{org}}$  values, and an increase in TOM at 7.0 kyr B.P. lags behind a large decrease in  $\delta^{18}\text{O}_{\text{calcite}}$  values beginning at 7.3 kyr B.P. We interpret these changes as a drying event, similar to the 8.2 ka event, with a change in the source of atmospheric vapor and/or an increase in winter derived precipitation (Diefendorf et al. 2006). During this interval, the decrease in  $\delta^{13}\text{C}_{\text{org}}$  values would be forced by a transition from an open to closed lake system, consistent with a decrease in flux of WC. A similar event is also observed in Seneca Lake sediment in the northeastern United States at  $\sim 7$  ka (Guiles-Ellis et al. 2004). To our knowledge, this event is not observed elsewhere; however, we argue that a perturbation in atmospheric circulation occurred at this time that resulted in the observed changes at Lough Inchiquin.

## Conclusions

Lough Inchiquin sediment provides a continuous archive of late-glacial and Holocene changes in

landscape evolution and climate change. This study utilizes wt. % total calcite, wt. % total organic matter, C/N ratios, lithostratigraphic characteristics,  $\delta^{13}\text{C}_{\text{org}}$ ,  $\delta^{13}\text{C}_{\text{calcite}}$ , and  $\delta^{13}\text{C}$  values of various of modern plants, and  $\delta^{13}\text{C}$  values of limestone bedrock. Isotope excursions in lacustrine sediment records are controlled by a myriad of factors including: aquatic productivity, aquatic respiration, algal isotope fractionation, hydrology, atmospheric exchange, and exogenous sources of carbon including carbonate weathering and unoxidized terrestrial organic matter via particulate organic carbon or dissolved organic carbon. These factors complicate the interpretation of isotope excursions in lakes.

In this study, we present a model of carbon isotope systematics in a hard-water lake to characterize changes using Lough Inchiquin  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values. During the late glacial and early Holocene exogenous sources of carbon dominate lake water  $\delta^{13}\text{C}_{\text{DIC}}$  values as the terrestrial landscape transitions from exposed limestone bedrock to a vegetated surface. This results in a dramatic change in the  $\delta^{13}\text{C}$  values of weathered carbon entering the lake from a bedrock signal of  $\sim 3.4\%$  VPDB to an oxidized soil organic matter values ( $-25$  to  $-30\%$  VPDB). Exogenous sources of carbon in lake systems are generally not considered important in studies of carbon cycling in lakes. We argue that exogenous sources of carbon exert a significant and often dominant control on lake water  $\delta^{13}\text{C}_{\text{DIC}}$  values. This has profound implications for development of paleoclimate records from lacustrine sediment and we contend that the selection of appropriate lakes can result in paleoclimate records of terrestrial evolution where other terrestrial records are not available.

## Supplementary information available

Supplementary information to this article can be found in the online version of this article at [www.springerlink.com](http://www.springerlink.com).

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## References

- Alley RB, Mayewski PA, Sowers T, Stuiver M, Taylor KC, Clark PU (1997) Holocene climatic instability: a prominent, widespread event 8,200 yr ago. *Geology* 25:483–486
- Allott NA (1986) Temperature, oxygen and heat-budgets of six small western Irish lakes. *Freshwater Biol* 16:145–154
- Arthur MA, Dean WE, Claypool GE (1985) Anomalous  $^{13}\text{C}$  enrichment in modern marine organic carbon. *Nature* 315:216–218
- Bade DL, Carpenter SR, Cole JJ, Hanson PC, Hesslein RH (2004) Controls of  $\delta^{13}\text{C}$ -DIC in lakes: geochemistry, lake metabolism, and morphometry. *Limnol Oceanogr* 49:1160–1172
- Baldini JUL, McDermott F, Fairchild IJ (2002) Structure of the 8,200-year cold event revealed by a speleothem trace element record. *Science* 296:2203–2206
- Blair NE, Leithold EL, Ford ST, Peeler KA, Holmes JC, Perkey DW (2003) The persistence of memory: the fate of ancient sedimentary organic carbon in a modern sedimentary system. *Geochem Cosmochim Acta* 67:63–73
- Cerling TE (1984) The stable isotope composition of modern soil carbonate and its relationship to climate. *Earth Planet Sc Lett* 71:229–240
- Cerling TE (1999) Stable carbon isotopes in palaeosol carbonates. *Sp Pubs Int Assoc Sedimentol* 27:43–60
- Dean WE (1974) Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *J Sediment Petrol* 44:242–248
- Dickinson CH, Pearson MC, Webb DA (1964) Some microhabitats of the Burren, their microenvironments and vegetation. *Proc Roy Irish Acad* 63B:291–302
- Diefendorf AF (2005) Late-Glacial to Holocene climate variability in western Ireland. Department of Geological Sciences. University of Saskatchewan, Saskatoon, Saskatchewan, p 125
- Diefendorf AF, Patterson WP, Mullins HT, Tibert N, Martini A (2006) Evidence for high-frequency late Glacial to mid-Holocene (16,800 to 5,500 cal yr B.P.) climate variability from oxygen isotope values of Lough Inchiquin, Ireland. *Quat Res* 65:78–86
- Drew DP (1983) Accelerated soil erosion in a karst area: the Burren, western Ireland. *J Hydrol* 61:113–124
- Drew DP (1988) The hydrology of the Upper Fergus River catchment, Co. Clare *Proc Univ Bristol* 18:265–277
- Ehleringer JR, Buchmann N, Flanagan LB (2000) Carbon isotope ratios in belowground carbon cycle processes. *Ecol Appl* 10:412–422
- Farquhar GD, Ehleringer JR, Hubick KT (1989) Carbon isotope discrimination and photosynthesis. *Annu Rev Plant Phys Plant Mol Biol* 40:503–537
- Glaser B (2005) Compound-specific stable-isotope ( $\delta^{13}\text{C}$ ) analysis in soil science. *J Plant Nutr Soil Sci* 168:633–648
- Gleixner G (2005) Stable isotope composition of soil organic matter. In: Flanagan L, Ehleringer JR, Pataki DE (eds) *Stable isotopes and biosphere-atmosphere interactions: processes and biological controls*. Elsevier Academic Press, New York, pp 29–46
- Guiles-Ellis K, Mullins HT, Patterson WP (2004) Deglacial to middle Holocene (16,600 to 6,000 calendar years BP) climate change in the northeastern United States inferred from multi-proxy stable isotope data, Seneca Lake, New York. *J Paleolimnol* 31:343–361
- Hammarlund D, Aravena R, Barnekow L, Buchardt B, Possnert G (1997) Multi-component carbon isotope evidence of early Holocene environmental change and carbon-flow pathways from a hard-water lake in northern Sweden. *J Paleolimnol* 18:219–233
- Hedges JJ, Oades JM (1997) Comparative organic geochemistries of soils and marine sediments. *Org Geochem* 27:319–361
- Hollander DJ, McKenzie JA (1991)  $\text{CO}_2$  control on carbon-isotope fractionation during aqueous photosynthesis: a paleo- $p\text{CO}_2$  barometer. *Geology* 19:929–932
- Hollander DJ, McKenzie JA, Haven H (1992) A 200 year sedimentary record of progressive eutrophication in Lake Greifen (Switzerland): implications for the origin of organic-carbon-rich sediments. *Geology* 20:825–828
- Indermühle A, Stocker TF, Joos F, Fischer H, Smith HJ, Wahlen M, Deck B, Mastroianni D, Tschumi J, Blunier T, Meyer R, Stuaffer B (1996) Holocene carbon-cycle dynamics based on  $\text{CO}_2$  trapped in ice at Taylor Dome, Antarctica. *Nature* 398:121–126
- Irvine K, Allott NA, Caroni R, DeEyto E, Free G, White J (2001) Ecological assessment of Irish lakes. The development of a new methodology suited to the needs of the directive on surface waters. Environmental Protection Agency, Ardcavan, Co. Wexford, Ireland
- Isarin RFB, Renssen H, Koster EA (1997) Surface wind climate during the Younger Dryas in Europe as inferred from aeolian records and model simulations. *Palaeogeogr Palaeoclimatol* 134:127–148
- Jones RI, Grey J, Sleep D, Quarmby C (1998) An assessment, using stable isotopes, of the importance of allochthonous organic carbon sources to the pelagic food web in Loch Ness. *Proc: Biol Sci* 265:105–111
- Kump LR, Arthur MA (1999) Interpreting carbon-isotope excursions: carbonates and organic matter. *Chem Geol* 161:181–198
- Laws EA, Popp BN, Bidigare RR, Kennicutt MC, Macko SA (1995) Dependence of phytoplankton carbon isotopic composition on growth rate and  $[\text{CO}_2]_{\text{aq}}$ : theoretical considerations and experimental results. *Geochem Cosmochim Acta* 59:1131–1138
- MacDermot CV, Pracht M, McConnell BJ (2003) Geology of Galway bay: sheet 14. Geological Survey of Ireland
- Magny M, Begeot C (2004) Hydrological changes in the European midlatitudes associated with freshwater out-

- bursts from Lake Agassiz during the Younger Dryas event and the early Holocene. *Quat Res* 61:181–192
- McConnaughey TA (1991) Calcification in *Chara corallina*: CO<sub>2</sub> hydroxylation generates protons for bicarbonate assimilation. *Limnol Oceanogr* 36:619–628
- McConnaughey TA, Falk RH (1991) Calcium-proton exchange during algal calcification. *Biol Bull* 180:185–195
- McDermott F, Matthey DP, Hawkesworth C (2001) Centennial-scale Holocene climate variability revealed by a high-resolution speleothem  $\delta^{18}\text{O}$  record from SW Ireland. *Science* 294:1328–1331
- McKenzie JA (1985) Carbon isotopes and productivity in the lacustrine and marine environment. In: Stumm W (ed) *Chemical processes in lakes*. Wiley, New York, pp 99–118
- Meyers PA, Ishiwatari R (1993) Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org Geochem* 20:867–900
- Mook WG (1986) <sup>13</sup>C in atmospheric CO<sub>2</sub>. *Neth J Sea Res* 20:211–223
- Mook WG, Bommerson JC, Staverman WH (1974) Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet Sci Lett* 22:169–176
- O’Connell M, Huang CC, Eicher U (1999) Multidisciplinary investigations, including stable-isotope studies, of thick Late-glacial sediments from Tory Hill, Co. Limerick western Ireland. *Palaeogeogr Palaeoclimatol Paleoclimatol* 147:169–208
- O’Leary MH (1981) Carbon isotope fractionation in plants. *Phytochemistry* 20:553–567
- Pace ML, Cole JJ, Carpenter SR, Kitchell JF, Hodgson JR, Van de Bogert MC, Bade DL, Kritzberg ES, Bastviken D (2004) Whole-lake carbon-13 additions reveal terrestrial support of aquatic food webs. *Nature* 427:240–243
- Popp BN, Laws EA, Bidigare RR, Dore JE, Hanson KL, Wakeham SG (1998) Effect of phytoplankton cell geometry on carbon isotopic fractionation. *Geochem Cosmochim Acta* 62:69–77
- Quade J, Cerling TE, Bowman JR (1989) Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along elevation transects in the southern Great Basin, United States. *Geol Soc Am Bull* 101:464–475
- Quay PD, Emerson SR, Quay BM, Devol AH (1986) The carbon cycle for Lake Washington—a stable isotope study. *Limnol Oceanogr* 31:596–611
- Royer DL, Berner RA, Beerling DJ (2001) Phanerozoic atmospheric CO<sub>2</sub> change: evaluating geochemical and paleobiological approaches. *Earth-Sci Rev* 54:349–392
- Santruckova H, Bird MI, Lloyd J (2000) Microbial processes and carbon-isotope fractionation in tropical and temperate grassland soils. *Funct Ecol* 14:108–114
- Sauer PE, Miller GH, Overpeck JT (2001) Oxygen isotope ratios of organic matter in arctic lakes as a paleoclimate proxy: field and laboratory investigations. *J Paleolimnol* 25:43–64
- Stuiver M, Reimer PJ, Bard E, Beck JW, Burr GS, Hughen KA, Kromer B, McCormac G, Van Der Plicht J, Spurk M (1998) INTCAL98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40:1041–1083
- Talbot MR (1990) A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chem Geol* 80:261–279
- Talbot MR (2001) Nitrogen isotopes in palaeolimnology. In: Last WM, Smol JP (eds) *Tracking environmental change using lake sediments*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp 401–439
- Watts WA (1963) Late-glacial pollen zones in western Ireland. *Irish Geogr* 4:367–376
- Watts WA (1984) The Holocene vegetation of The Burren, western Ireland. In: Haworth EY, Lund JWG (eds) *Late sediment and environmental history*. University of Minnesota Press, Minneapolis, pp 155–185
- Watts WA (1985) Quaternary vegetation cycles. In: Edwards KJ, Waten WP (eds) *The quaternary history of Ireland*. Academic Press, London, pp 155–185